

Advanced Lightweight Multifunctional Materials

1. Additive manufacturing of multifunctional materials

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In the last decade, there have been significant advances on multifunctional materials development through additive manufacturing techniques, boosted by the Industry 4.0 and the Internet of Things revolution. However, in the particular case of the use of lightweight materials, the performance and multifunctionality is sometimes limited. After a short introduction, this chapter provides a comprehensive assessment of those limitations at the same time as the materials, techniques and challenges on the additive manufacturing of multifunctional materials. In the final paragraphs of this work, the future trends will be presented and discussed.

1. Introduction

Additive manufacturing has strongly grown over the last 30 years. After being introduced in 1986 by Charles Hull with respect to the stereolithography (SLA) process, it has emerged from the mere proof-of-concept in prototyping into viable fabrication alternatives for end-use parts¹⁻².

Additive manufacturing technologies are effectively used in a wide range of applications in areas such as automotive³, aerospace⁴, consumer products⁵, biomedical engineering⁶, architecture⁷, and energy generation and storage⁸, among others⁹⁻¹².

Several methods of additive manufacturing (Figure 1) have been established to meet the demands of printing complex structures at fine resolutions, including rapid prototyping, fused deposition modelling (FDM), selective laser sintering (SLS), selective laser melting (SLM), liquid binding in three-dimensional printing (3DP), as well as printing technologies, contour crafting, stereolithography, direct energy deposition (DED) and laminated object manufacturing (LOM)¹³.

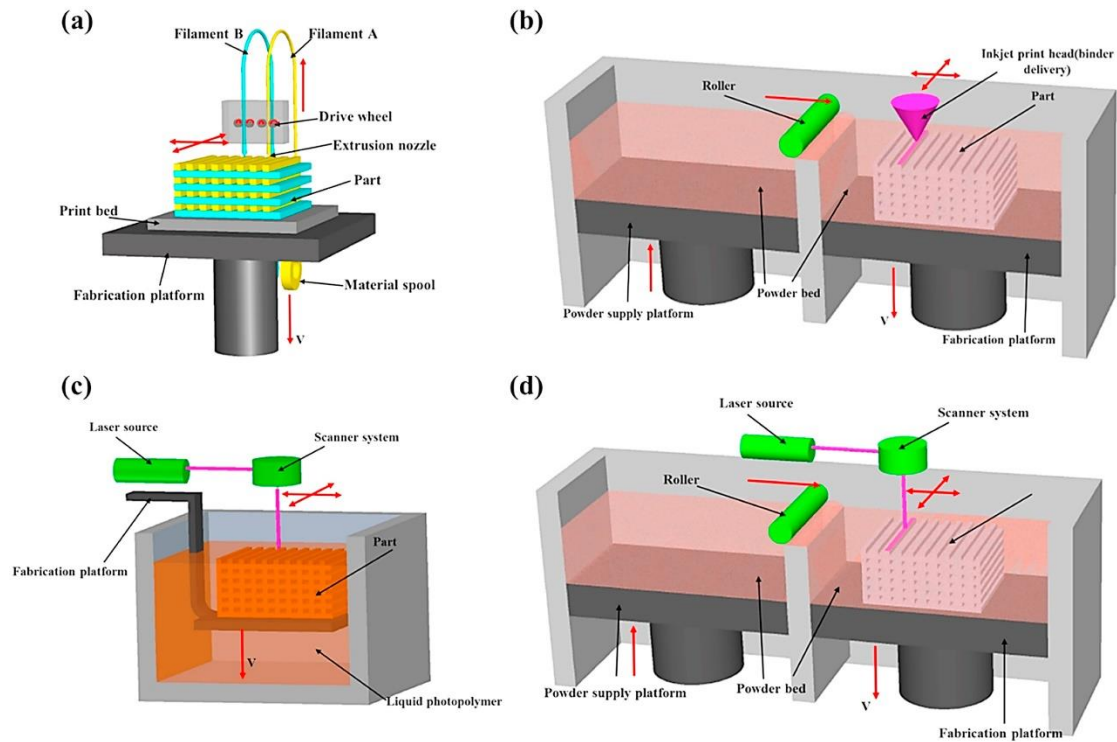


Figure 1. Schematic representation of the some of the main methods of additive manufacturing: (a) fused deposition modelling; (b) inkjet printing; (c) stereolithography; (d) powder bed fusion. Reproduced with permission from ¹⁴.

All these techniques are being used in an increasing number of industries in areas ranging from rapid prototyping, toolmaking and production of smart and multifunctional components, key technologies for industry 4.0 as well as for the Internet of Things revolution¹⁵.

Additive manufactured multifunctional materials are designed to perform a variety of functions apart from the primary functions, removing the need of different integrated components, by combining one or more functional capabilities of subsystems within the materials structure, so that the system mass and volume can be reduced, improving also the overall efficiency of the system¹⁶. Such materials can perform multiple structural functions or both structural (strength, stability and stiffness, among others) and non-structural functions (energy harvesting, self-healing, sensing and actuations, among others). Non-structural functions can include sensing, electromagnetic interference, heating, energy generation, energy storage, actuation and self-healing (Figure 2)¹⁷⁻¹⁸.

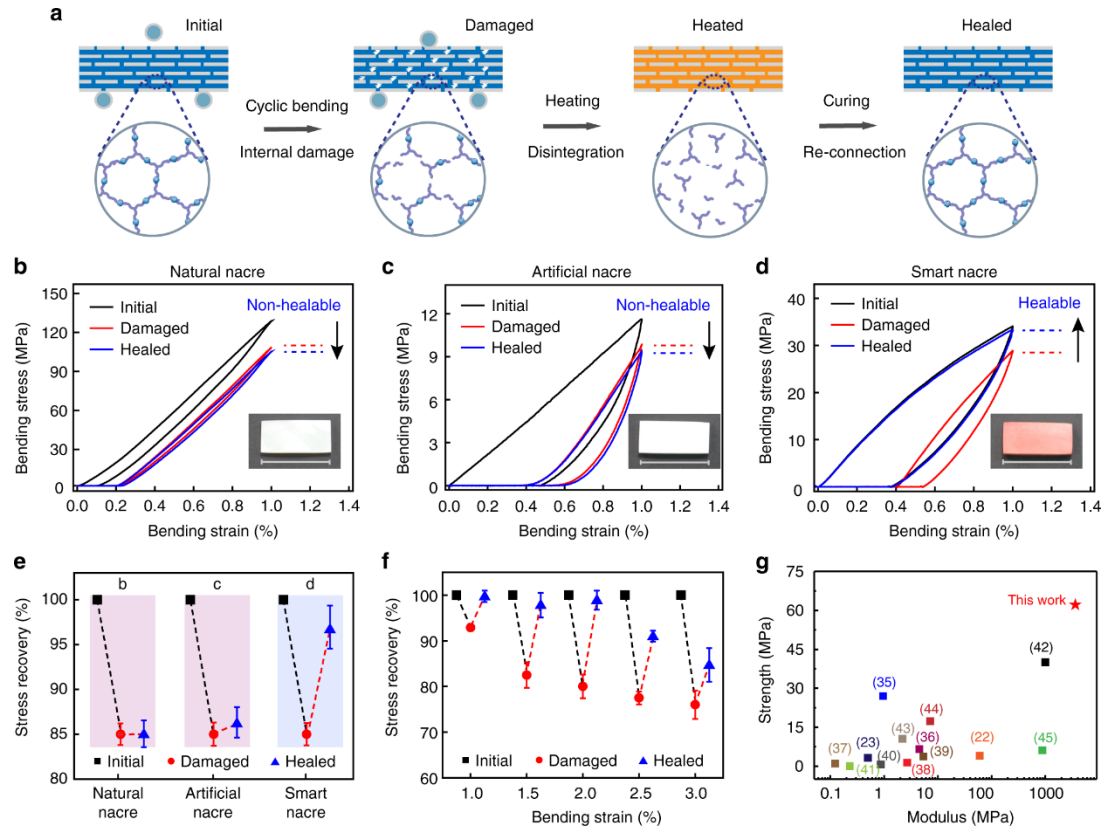


Figure 2. Self-healing mechanism of smart nacre and its mechanical recovery behaviour. (a) Schematic illustration of the damage-healing process of smart nacre. Stress-strain curves recorded during the damage-healing process for a natural nacre (b), an artificial nacre infiltrated with non-healable polymer (c), and smart nacre (d). Insets are the optical images for the corresponding samples. (e) Summary of the normalized strength for the initial, damaged, and healed specimens for the three types of samples in b–d. Summary of the normalized strength for the initial, damaged, and healed smart nacre, when damaged under different bending strain (f). (g) Ashby chart summarizing the strength vs. modulus of various self-healable materials. Error bars represent standard deviations calculated from five specimens. Scale bar in b–d is 2 cm. Reproduced with permission from¹⁸.

Lightweight materials, particularly polymers, offer unique properties for printable multifunctional materials technologies, namely their low-cost, low density, high strength, modulus of elasticity, high versatility when compared to inorganic materials, high flexibility, simple fabrication techniques and the possibility of being produced in a variety of substrates. Additionally, there is also the widespread possibility of tailoring side-chains and molecular structure of those lightweight materials, introducing charged/neutral fillers, as well as introducing particles with specific properties into the material in bulk

(polymer composites), enabling materials to be fabricated with specific chemical and physical properties¹⁹.

This chapter will present a short introduction on the main aspects of additive manufacturing of polymer based lightweight multifunctional materials: research scenario, materials, techniques, limitations and challenges.

2. Research scenario

2.1 Materials Development

One of the first studies on the «additive manufacturing of lightweight multifunctional materials» topic was reported in 2004 by Burrows *et al.*²⁰, addressing the migration of unreacted photoinitiators and their by-products from UV-cured printed materials and coatings, a major issue in food packaging applications. This study shows multifunctional photoinitiators that involve the attachment of photoinitiators with reactive functional groups to a multifunctional core.

Five years later and due to the increasing demand for biocompatible coatings that can be simultaneously used for the display of biologically active compounds on a background displaying low nonspecific interaction, Mahaveer *et al.*²¹ demonstrated the successful coating of glass slides with random copolymers of glycidyl methacrylate and poly(ethylene glycol) methacrylate. Additionally, printing conditions of a calligrapher printer were optimized for a fluorescently labelled model protein, regarding the temperature, humidity, pin geometry, concentration, and pH of the printing solution. In the same year, it was introduced the idea of a multifunctional composite laminates which can harvest and store solar energy²². The idea was materialized through an amorphous silicon solar cell and a thin film solid state lithium-ion battery that were adhesively joined and electrically connected to a thin flexible printed circuit board. Then, the passive components such as resistors and diodes were electrically connected to the printed circuit board with silver paste (Figure 3).

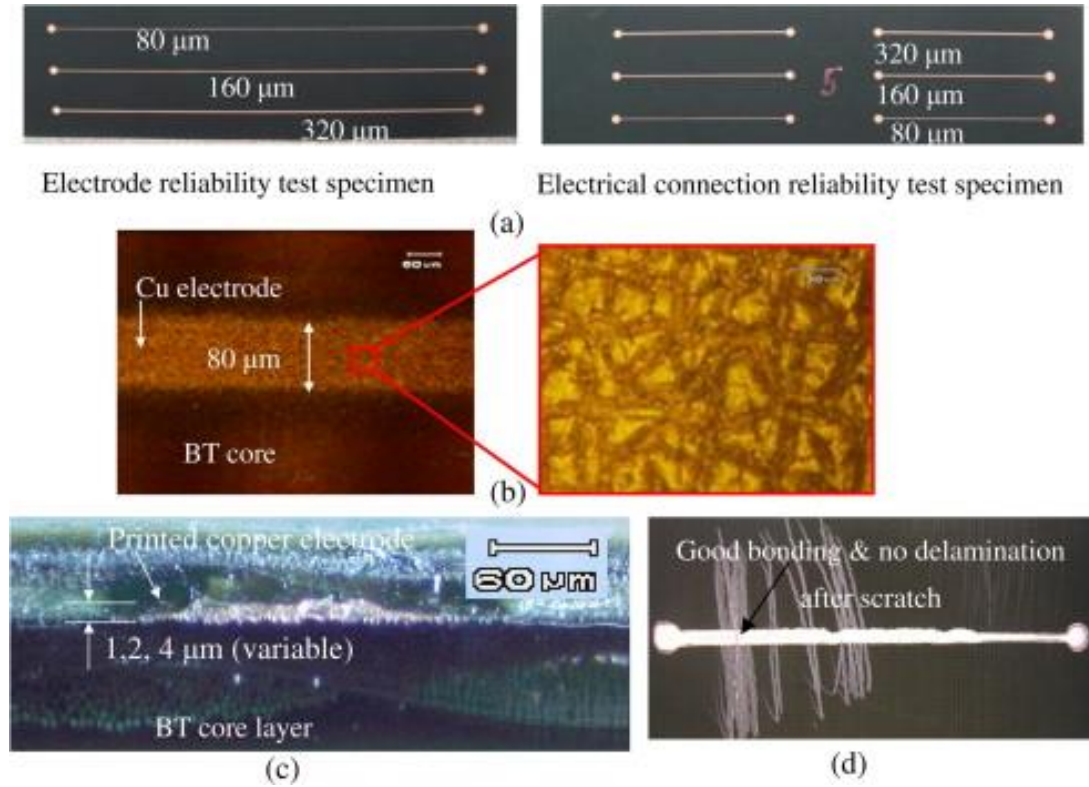


Figure 3. Printed copper electrode: (a) photograph; (b) optical microscope top view; (c) cross-section view of the printed electrode; (d) experiment results of a scratch test using a diamond-tip pen. Reproduced with permission from²².

The integrated printed circuit board was ink-jet printed and co-cured with graphite/epoxy to fabricate an energy harvesting/storage multifunctional composite. With respect to energy storage, Gonçalves *et al.*²³ reported the development of printed electrodes through screen-printing with an ink formulation developed from a green solvent, a polymer binder, and graphite (anode) or C-LiFePO₄ (cathode). The morphology of the electrodes is homogeneous, and in relation to the electrochemical performance, the discharge capacity value for the cathode film with poly(styrene-butene/ethylene-styrene) (SEBS) and PVDF binders is 137 and 53 mA h g⁻¹ at C/5 and 113 and 29 mA h g⁻¹ at 5C, respectively, revealing in this way adequate cycling performance and suitability for printed lithium-ion batteries. By using the same technique, Costa *et al.*²⁴ developed polymer blends based on polyaniline and thermoplastic elastomer styrene-ethylene/butylene-styrene (SEBS) copolymer showing large strain yield (>10% for 40 wt% PANI content), high electrical conductivity, 1 S/m, after the percolation threshold at \approx 10 wt% PANI and suitable piezoresistive response with gauge factor (GF) between \approx

1.5 and 2.4 for deformations up to 10%. suitable for advanced electromechanical sensors applications.

With the mixing of ceramic/polymers and nano-sized active filler particles, it was achieved the fabrication of polymer-derived silicate ceramics in various shapes and with variable composition, with potential applications in the fabrication of components suitable for biological, high temperature and functional applications²⁵. Three types of silicone resins (Silres® MK, Silres® H44 and Silres® H₆₂C, Wacker-Chemie GmbH, München, Germany), two types of polysilazanes (Ceraset PSZ20, and perhydropolysilazane) and two types of fillers (TiO₂ nano-sized powder and Eu₂O₃ nanoparticles) were used. Shaping of the components was carried out using several plastic forming technologies, such as warm pressing, extrusion, injection molding, foaming, machining, fused deposition and 3D printing.

Other additive manufacturing technique, solvent-cast direct-writing, offers a low-cost, highly flexible and powerful fabrication route for microsystems featuring mechanical, microfluidic and/or electrical functionalities, by using a thermoplastic polylactide polymer solution ink with dichloromethane²⁶. Materials were processed by robotically controlled microextrusion of a filament combined with rapid solvent evaporation (Figure 4).

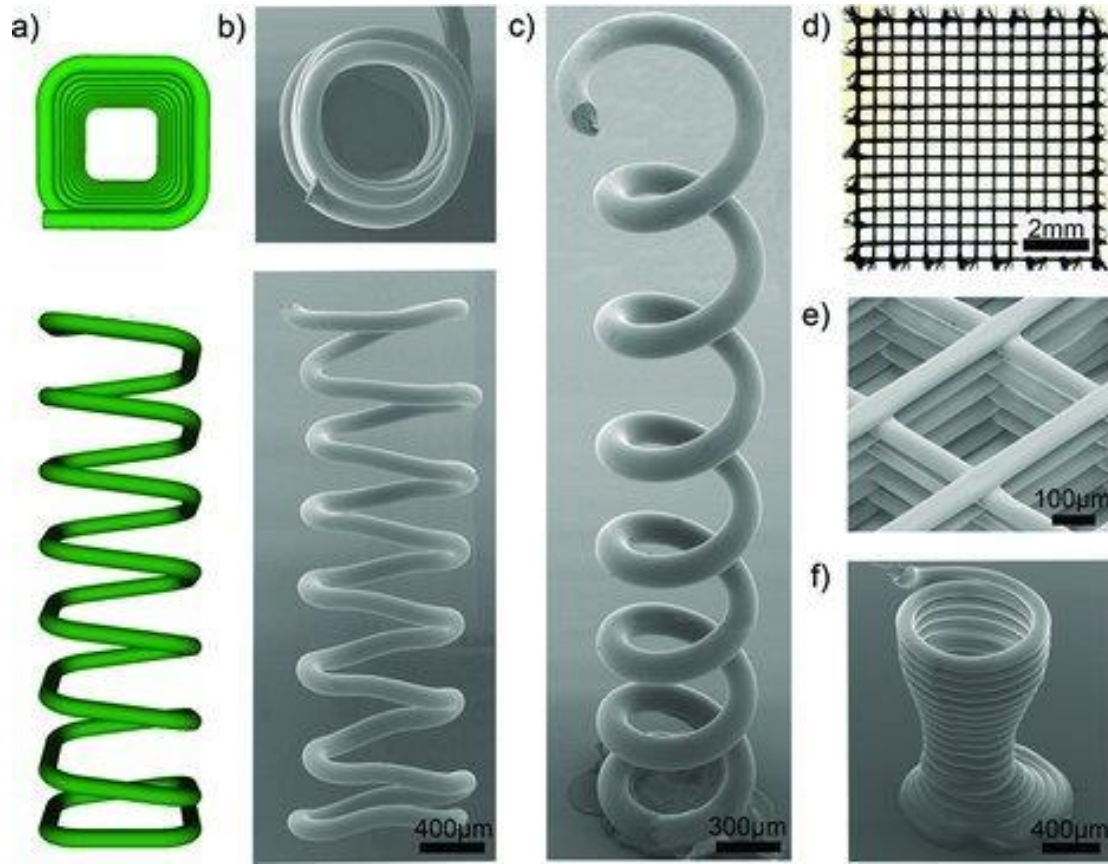


Figure 4. Microstructures manufactured by solvent-cast direct-writing. (a) Top and side view virtual images of the programmed solvent-cast direct-writing fabrication of the square spiral. (b) Top and side view SEM images of a PLA square spiral. (c) Inclined top view SEM image of a PLA circular spiral. (d) Representative optical image of a PLA scaffold composed of nine layers. (e) Inclined top view SEM image of PLA 9-layer scaffold. (f) SEM image of a PLA cup. Reproduced with permission from²⁶.

Upon drying, the increased rigidity of the extruded filament enables the fabrication of complex freeform 3D shapes (high-toughness fibers, spiral microchannels and antennas).

Melt electrowriting²⁷ with additive manufacturing principles was also developed, the experimental setup uses an electric field to generate a stable fluid jet with a expectable path, that is uninterruptedly deposited onto a collector. The resulting fiber diameter is variable during the process and has potential for the biomedical field, providing a unique opportunity to perform low-cost, high resolution, additive manufacturing research that is well positioned for clinical translation, using existing regulatory frameworks²⁸.

Xu *et al.*²⁹ reported the development of 3D elastic silicone elastomer-based membranes shaped to match the epicardium of the heart via 3D printing, as a platform for

deformable arrays of multifunctional sensors, electronic and optoelectronic components. Such devices completely envelop the heart, in a form-fitting way, and possess inherent elasticity, providing a mechanically stable biotic/abiotic interface during normal cardiac cycles. Semiconductor materials including silicon, gallium arsenide and gallium nitride, co-integrated with metals, metal oxides and polymers, provide the multifunctional capability. Still in the field of membranes, Gao *et al.*³⁰, presented a combined inkjet printing and template synthesis technique to prepare charge mosaic membranes in a rapid and straightforward manner, demonstrating the unique transport properties that result from the mosaic membrane design. For that, poly(vinyl alcohol) based composite inks containing poly(diallyldimethylammonium chloride) or poly(sodium 4-styrenesulfonate) were used to pattern positively-charged or negatively-charged domains, respectively, on the surface of a polycarbonate track-etched membrane with 30 nm pores. The developed membranes can be deployed in nanoscale technologies that rely on the selective transport and separation of ionic solutes from solution.

In a theoretical study³¹ by numerical simulations it was discussed the idea that the multifunctional response of a polymeric systems (acrylonitrile butadiene styrene and polylactic acid) can be manipulated by axial grading and that optimal design/fabrication of multifunctional smart structures by 3D printing may be developed for vibration control applications. Most importantly, such modelling and resulting solutions framework can also be used for analysing the vibration of the structures, showing that smart materials can be incorporated for axial grading and may be manipulated for vibration control applications.

Polylactic acid was also used by Prashantha *et al.*³² as a matrix for graphene aiming to allow additive multilayer deposition of the polymeric multifunctional nanocomposite. The resulting 3D printed polylactic acid/graphene nanocomposites containing 10 wt.% graphene in PLA matrix exhibited improved mechanical and thermo-mechanical properties, becoming a promising new 3D printable biomaterial for tissue engineering, bioelectronics and biosensors.

Keeping the focus on polymer-based graphene nanocomposites, Yamamoto *et al.*³³ addressed the problems of fused filament fabrication or fused deposition modelling, namely the low strength and toughness of the typical thermoplastic materials such as acrylonitrile butadiene styrene, polylactic acid, and polybutylene terephthalate. For that, the team introduced 0.06 wt.% of graphene oxide on a acrylonitrile butadiene styrene matrix, that lead to a much higher strain-to-failure (14% for facedown and 29% for

upright) and toughness (20% for facedown and 55% for upright) while also increasing the fracture strength (3.5% for facedown and 10% for upright) and decreasing the stiffness (6% for facedown and 15% for upright). Such improvements in strain-to-failure, toughness, and fracture strength have shown the multifunctionality of the developed printed system where several mechanical properties are improved for a number of structural applications.

Unique properties including controlled surface slipperiness, self-reporting on the loss of liquid repellency and sensing the temperature of contacting liquids, demonstrated on the printed nanocomposites with lubrication treatment were reported on ultrahigh-molecular-weight polyethylene/SiO₂ nanocomposites³⁴.

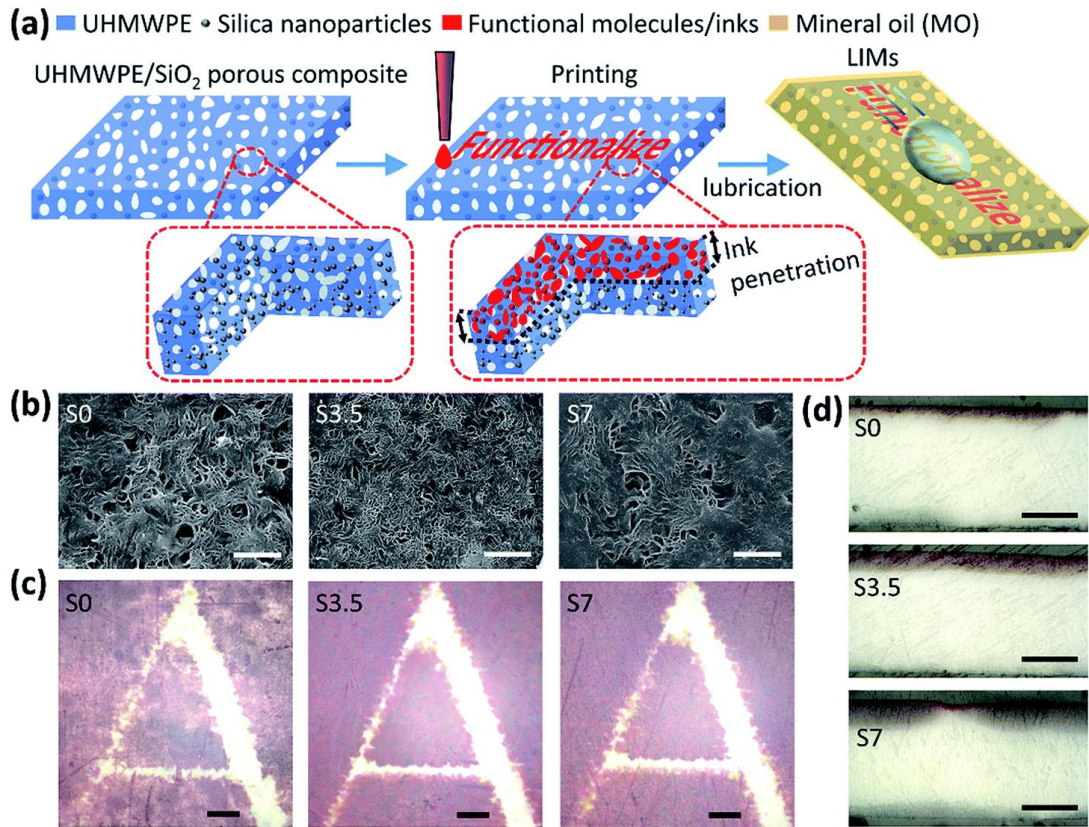


Figure 5. (a) Schematic representation of print-assisted functionalization on porous nanocomposites for multifunctional liquid-infused materials. (b) Surface morphology of UHMWPE/SiO₂ nanocomposites with different SiO₂ contents. (c) Optical images of the corresponding UHMWPE/SiO₂ nanocomposites after ink-jet printing. (d) Cross section of Printed-S0, Printed-S3.5 and Printed-S7 samples showing distinct ink penetration depth. Scale bar: (b) 5 μ m; (c) 300 μ m; (d) 200 μ m. Reproduced with permission from³⁴.

The functional printing of ultrahigh-molecular-weight polyethylene/SiO₂ nanocomposites was performed by using a commercial-available ink-jet printer (L801, Epson, Japan) and shows applicability in anti-fouling coatings, food/medical packaging, smart windows and sensors.

While many “ad hoc” designs of 4D printed solutions have been progressively developed for specific processes, the general approach to produce smart materials by additive manufacturing techniques, in real time across an entire product development process, is not pervasive in the industry. To solve this issue, Jian *et al.*³⁴ proposed a general 4D printing oriented framework for the design of multi-functional shape-memory polymer architectures. Such report was not intended to be an exhaustive and specific instruction but is instead a means to motivate to seek the process for applying these unique functional materials for specific designs and applications.

Multiwall carbon nanotubes were found to improve the electrical and dielectric properties, to promote ultrahigh polarization density and to form local micro-capacitors within poly(vinylidene) fluoride/BaTiO₃ composites³⁵. Additionally, the 3D printing process of those materials provided homogeneous dispersion of nanoparticles, alleviating agglomeration of nanoparticles, and reducing the micro-crack/voids in the matrix. Such promising results opened the way for the 3D printing of multifunctional nanocomposites with temperature and strain sensing capabilities, increased mechanical property, as well as the feasibility for large-scale multifunctional sensor device manufacturing with freedom of design and low-cost.

By mixing materials that are simultaneously electroactive and magnetoactive, and knowing that the successful application of those magnetoelectric materials is closely related to the processing and integration additive manufacturing techniques, Lima *et al.*³⁶ developed novel screen-printed and flexible ME materials composed of poly(vinylidene fluoride-co-trifluoroethylene) P(VDF-TrFE) as the piezoelectric phase and poly(vinylidene fluoride)(PVDF-CFO) as the magnetostrictive one. Such all-printed ME composite exhibited a ME voltage coefficient (α) of 164 mV cm⁻¹ Oe⁻¹ at a longitudinal resonance frequency of 16.2 kHz.

The optimized magnetic, piezoelectric and ME behaviour, together with the reduced cost of assembly, easy integration into devices and the possibility of being obtained over flexible and large areas through additive manufacturing techniques,

demonstrated the suitability of the advanced lightweight multifunctional materials for applications in printed electronics, sensors, actuators, and energy harvesters (Figure 6).

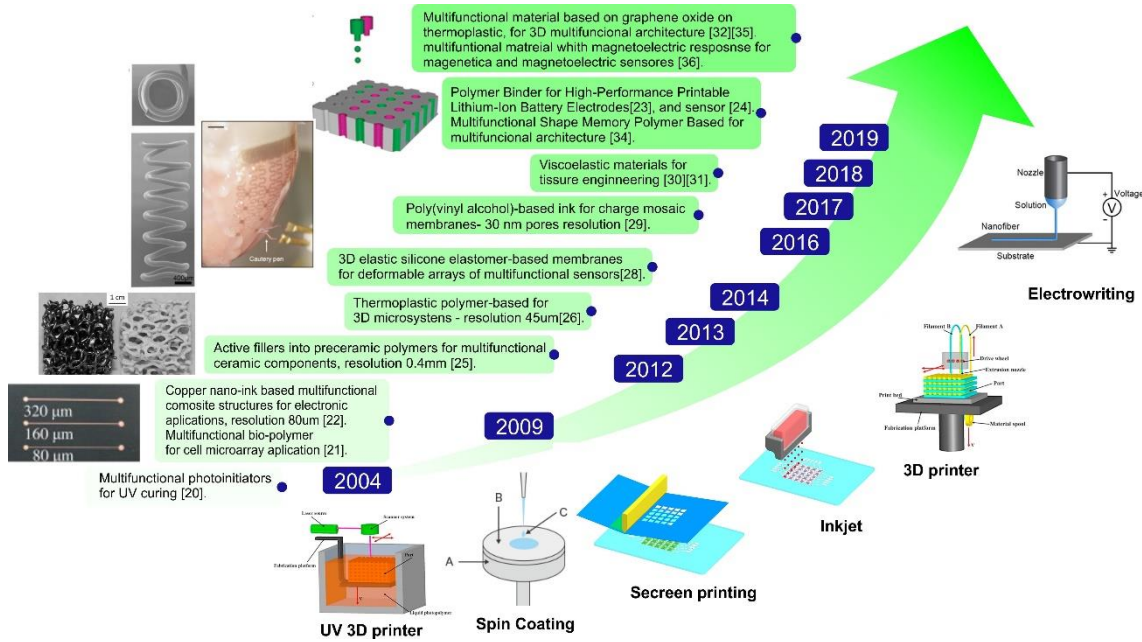


Figure 6. Schematic summary of the evolution of the development of multifunctional materials through additive manufacturing techniques.

2.2 Materials for electronics

Electronic systems, and the whole area of electronics in general, have shown exponential growth in recent decades, as demonstrated by a simple technological comparison between the current date and the past decade. This evolution is supported by a correlated growth in advanced materials, with particular focus on the last decade in (multi)functional materials. This combination of extremely efficient and miniaturized electronic systems and ever-performing functional materials makes it possible to move to new and exciting research scenarios.

While being the interaction of these two worlds not yet easy, the evolution of additive manufacturing systems allows this combination to become increasingly easy, thus reaching solutions previously imaginable in terms of integration, flexibility, size and autonomy.

By examining the domains of additive manufacturing within the electronics industry, it is realized that inkjet printing techniques are increasingly being used to produce electronic systems, including circuit boards. Typically, this method involves a printhead that works on a horizontal surface by applying conductive inks that allow the rapid production of

custom circuit boards. However, a big revolution is expected and corresponds to the complete manufacturing of electronic circuitry, electronic components and the structural part of the device, resulting in a fully functional product digitally fabricated by purely additive processes.

Thus, research in this field is further developing this concept, where specific works are pointing out this way, as it is the case of printed organic transistors (OTFTs), reported of since 2002³⁷. Most of these reports make use of flexible substrates, but the fabrication is based on subtractive technology. The fabrication of fully printed OTFTs has been also reported, such as in Castro *et al.*³⁸, where a bottom-gate approach is used to print fully functional 4-layer inkjet-printed OTFTs, the device being characterized by an electron mobility of $0.012 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratio of 103. More recently, higher performance has been achieved by improving both active materials and printing technologies, the actual main challenge being the manufacturing success rate versus device efficiency³⁹, as only then the devices will become interesting for industrial applications.

Another major field of development in the field of printed electronics involves the printing of OLEDs where one of the solutions developed to maximize performance is the use of light emitters, inorganic or hybrid materials, such as inorganic QDs and inorganic fluorescent dyes.

Singh *et al.*⁴⁰ demonstrated the use of an hybrid organic-inorganic material and inkjet printing for the fabrication of the emitting layer. It was shown that the device exceeded 10 kcd m^{-2} for rigid substrates and 9.6 kcd m^{-2} for flexible substrates, respectively. A major reason for using LEDs is the increasing demand of digital displays. In this field, Haverinen *et al.*⁴¹ presented displays manufactured using QDs of different sizes on a full-control red, green and blue direct current graphics matrix with a brightness of 100 cd m^{-2} . Being the only disadvantage of using inorganic QDs materials their high cost⁴². Thus, CNTs are being explored also for developing display devices. Shigematsu *et al.*⁴³ demonstrated printed electrodes based on single-wall carbon nanotubes coated with phosphor as the counter-electrode for emissive displays fabricated using electrostatic inkjet technique.

The study and development of passive electronic components has also proven to be an area of strong research and need, always with the ultimate goal of achieving fully printed devices. V. Correia *et al.*⁴⁴ proved to be possible to design and print resistances, capacitors and coils with specific characteristics, solely through inkjet printing

techniques⁴⁵. The feasibility of stacking these devices has also been explored and demonstrated to increase the efficiency of the end devices per unit area, thus competing with traditional manufacturing methods.

Research on printed sensors is another major research focus, with physical sensors such as pressure, strain, magnetic field, and current, among others already being reported⁴⁶. Nevertheless, efforts have to be devoted to meet industrial demands, mainly due to the lack of functional materials capable of guaranteeing reproducibility and durability over time, a factor which the new generations of functional materials already is addressing⁴⁷. Finally, another high impact area, where once again functional materials are among the most suitable solution, corresponds to the energy area, with the batteries being printed along with the capacitors, the devices that by far show the best results. Gaikwad *et al.*⁴⁸ demonstrated high-potential fully printed batteries with polyvinyl alcohol and cellulose being used as a substrate and separator and KOH and ZnO solution as electrolyte. The electrodes were printed by stencil printing and based on Zinc and MnO₂. As a result, the dimension of the printed pattern depends on that of the stencil's mesh. The results showed that the initial open circuit potential of the entire battery was 14 V. Currently some companies in the traditional battery business already have fully printed market solutions⁴⁹.

From the presented overview it is confirmed the strong development of printed electronics based on lightweight materials, and the real dependence on the evolution of functional materials, as well as their implementation in industrial manufacturing processes.

3. Future trends

It has been shown that advanced lightweight multifunctional materials have already found uses in a large variety of technological devices, being the inherent flexibility of additive manufacturing technologies that allows to fabricate complex geometries with spatially varying distributions of phases that can be engineered to tailor mechanical and physical properties in a precise way⁵⁰. Nevertheless, and in a general way, such concept is still in its first steps. As it matures, and in an exciting Internet of Things context, it will be part of daily life. While smart materials science has typically focused on the development of functional materials based on inorganic components¹⁹, it is important to take into account that there are an increasing number of lightweight materials that have also shown multifunctional behaviour. Nevertheless, and despite the advantages

of combining the Internet of Things, the multifunctional smart materials and printing processing concepts, most of the current commercially available devices are not based on printing technologies. This multidisciplinary concept has a strong scientific and economic potential in this increasingly interesting field.

Considering their well-known advantages such as fast curing processes at room temperature with reduced volatile organic compound emissions, UV curable multifunctional materials are becoming of general research and implementation interest. Chromic, self-healing, shape memory, piezoresistive, or piezoelectric materials are just a few examples of them. Parameters such as viscosity, density, surface tension, and contact angle on different substrates are parameters need to be discussed/optimized in detail when these multifunctional materials are reported, once they strongly influence their processability and integration into applications. Furthermore, depending on the nanofillers employed, the multifunctionality can be also affected. Thus, obtaining optimized materials in terms of functionality/smart response as well as processability requires a deep understanding on the filler-polymer interaction. In this way, the potential solutions and/or new approaches that are being investigated include the use of polymer coated fillers, new filler dispersion techniques or new fillers more compatible with UV-curable resin (i.e., that are not affected by and do not affect the UV curing process)⁵¹.

It is also important to notice that additive manufacturing technologies can be used to produce a large combination of alloys, metals, ceramics and composites in different geometries. It is, however, this same flexibility that renders additive manufacturing technologies difficult to develop into reliable commercial products. Additionally the additive manufacturing optimization generally does not carry out from one process to another, making it very difficult to generalize operational principles for the various additive manufacturing technologies for the production of multifunctional materials, such as would be required by industry for proper operation of a reliable manufacturing line.⁵⁰

In the next years, 4D printing techniques will allow an innovative and disruptive effect in this field due to the quality, efficiency and performance of this technique. In the particular case of biomedical sciences, 4D printing will allow customised production for each individual patient, whose smart implants, tools, devices, organ printing, tissue engineering and self-assembling human scale biomaterials can be easily achieved in less time which has extensive benefit to the patients⁵⁰. Such approach will replace the conventional and limited scaffold production methods, leading to new possibilities in the biomedical field.

Additive manufacturing on the production of photodetectors and UV curable polymer-based multifunctional materials will allow applications for consumer electronics, with added advantages in their production such as fast curing at room temperature, space and energy efficiency, high-resolution patterns, and solvent-free formulations⁵¹.

The most interesting is that many of the applications or products related with multifunctional materials, where additive manufacturing can have a huge impact, are not listed in this chapter once they do not currently exist, as traditional engineering has limited adaptability/ability to meet the current design demands. As the hardware, software, and materials capabilities in additive manufacturing tailored for the production of multifunctional materials continue to develop, new materials, new architectures, new geometries and smart 3D/4D multifunctional objects will present new, challenging and exciting opportunities in the near future.

Everything else is a ... challenging innovation roadmap.

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